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METHOD FOR PRODUCING POLYESTER

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METHOD FOR PRODUCING POLYESTER

[Poriesuteru no seizoh houhoh]

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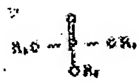
[There are no amendments to this patent.]

Claims /57*

1. In the production of a polyester by a polycondensation reaction for a glycol ester comprising at least one type of bifunctional aromatic carboxylic acid and/or a low grade polymer of same in the presence of a catalyst, a method for producing a polyester characterized by using the reaction product produced by reacting the phosphorus compound shown in general formula (III) below

* [The numbers in the right margin indicate pagination of the original text.]

 .... (III)

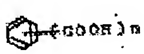
[In the formula, R_1, R_2, and R_3 are either hydrogen atoms or alkyl groups, and at least one of R_1, R_2, and R_3 is an alkyl group.]

with a reaction product A of the titanium compound shown in general formula (I) below

$Ti(OR)_4$ .... (I)

[In the formula, R is an alkyl group.]

and an aromatic polyhydric carboxylic acid shown in general formula (II) below

 .... (II)

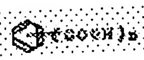
[In the formula, n is an integer in the range of 2-4.]
or an anhydride of the same as a polycondensation reaction catalyst.

2. The method for manufacturing polyester described in Claim 1 characterized by the fact that the reaction product A comprising the polycondensation reaction catalyst is a reaction product from a reaction between the titanium compound shown in general formula (I) below

$Ti(OR)_4$ .... (I)

[In the formula, R is an alkyl group.]

and 1/2-2 1/2 moles of an aromatic polyhydric carboxylic acid shown in general formula (II) below

 .... (II)

[In the formula, n is an integer in the range of 2-4.]
or an anhydride of the same added per 1 mole of the aforementioned titanium compound. /578

3. The method for manufacturing polyester described in Claim 1 or Claim 2 of the

invention characterized by the fact that the polycondensation reaction catalyst is a reaction product of product A and 1/3-6 moles of the compound shown in general formula (III) below

$$R_1O-\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle OR_3}{\underset{|}{P}}}}-OR_2 \quad \cdots\cdots\cdots\cdots (III)$$

[In the formula, R_1, R_2, and R_3 are either hydrogen atoms or alkyl groups, and at least one of R_1, R_2, and R_3 is an alkyl group.]
added to 1 mole of the titanium atoms included in the aforementioned reaction product A.

4. The method for manufacturing the polyester described in one of Claim 1 - Claim 3 characterized by the fact that the titanium compound used as a reactive component comprising the polycondensation reaction catalyst is a titanium compound shown in general formula (I') below.

$$Ti(OR')_4 \quad \cdots\cdots\cdots\cdots (I')$$

[In the formula, R' is an alkyl group with 3 or 4 carbon atoms.]

5. The method for manufacturing the polyester described in one of Claim 1 - Claim 4 characterized by the fact that the aromatic polyhydric carboxylic acid or the anhydride of same used as a reactive component comprising the polycondensation reaction catalyst is at least one compound selected from the group comprising phthalic acid, trimellitic acid, hemimellitic acid and pyromellitic acid and anhydrides of same.

6. The method for manufacturing the polyester described in one of Claim 1 - Claim 5 characterized by the fact that the phosphorus compound used as a reactive component comprising the polycondensation reaction catalyst is a phosphorus compound shown in general formula (II') below.

$$R_1'O-\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle OR_3'}{\underset{|}{P}}}}-OR_2' \quad \cdots\cdots\cdots\cdots (II')$$

[In the formula, R_1', R_2' or R_3' are either hydrogen atoms or alkyl groups with 1-4 carbon atoms, and at least one of R_1', R_2', and R_3' is an alkyl group with 1-4 carbon atoms.]

7. The method for manufacturing the polyester described in one of Claim 1 - Claim 6 characterized by the fact that the glycol ester of the bifunctional aromatic carboxylic acid is a glycol ester of terephthalic acid.

8. The method for manufacturing the polyester described in one of Claim 1 - Claim 6 characterized by the fact that the glycol ester of the bifunctional aromatic carboxylic acid is the ethylene glycol ester of terephthalic acid.

Detailed explanation of the invention

The present invention pertains to a method for manufacturing a polyester, and the invention further pertains to a method for manufacturing an aromatic polyester having a high softening point and excellent color.

Aromatic polyesters mainly comprising a bifunctional aromatic carboxylic acid and a glycol having excellent mechanical properties, physical properties, and chemical properties are widely used for fibers, films, and other molded articles. Among aromatic polyesters, a polyester having terephthalic acid as a primary acid component and ethylene glycol, tetramethylene glycol, hexamethylene glycol or cyclohexane-1,4-dimethylol as a glycol component is important.

The aforementioned polyesters, especially, polyethylene terephthalate, are produced by carrying out a polycondensation reaction for the ethylene glycol ester of terephthalic acid and/or a low grade polymer of same under heat and reduced pressure. The aforementioned polycondensation reaction progresses smoothly only when a catalyst is used and only then can a product with good product value be produced, and in this case, the reaction rate and quality of the product produced are strongly influenced by the type of catalyst.

As catalysts having superior performance in the polycondensation reaction, titanium compounds such as tetrabutyl titanate are well-known and have been used for a long time. However, when the aforementioned titanium compounds are used, yellowing of the polyester produced is likely to occur, and in particular, when a sufficient amount to accommodate an industrial production rate is used, the polyester produced has a deep yellow color, and furthermore, the softening point is reduced.

Methods to prevent the aforementioned coloring when a titanium compound is used have been proposed. In other words, a method in which hydrogenated titanium is used is disclosed in Japanese Kokoku Patent No. Sho 48[1973]-2229, and a method in which α-titanic acid is used is /579 disclosed in Japanese Kokoku Patent No. Sho 47[1972]-26597. However, forming hydrogenated titanium into a powder is not easy in the former method, and denaturing of α-titanic acid is likely to occur in the latter method, and storage and handling of the material are not easy and neither method is suitable for use on an industrial scale. Furthermore, a method in which a titanium salt of phosphorus acid is used is disclosed in Japanese Kokoku Patent No. Sho 43[1968]-9759, and a method in which a condensate of a titanium compound and phosphinic acid is used is disclosed in Japanese Kokai Patent Application No. Sho 48[1973]-49893. However, the aforementioned titanium-phosphorus compounds do not form a homogeneous and transparent catalytic solution,

and a solution containing a yellow-white deposit is formed. In order to produce a high quality polyester having a constant reaction rate, the quantitative addition of a very small amount of catalyst is essential, and formation of a uniform catalytic solution is very important from the standpoint of the handling ease of the catalyst. In particular, the formation of a uniform catalyst solution allows automatic measurement and addition of the catalyst, and is very important from the standpoint of industrial production. And furthermore, when an aforementioned titanium-phosphorus compound is used, the polyester produced exhibits significant, strong yellowing when the polycondensation reaction temperature is increased in order to increase productivity, and the product value is reduced sharply.

Based on the above background and as a result of much research conducted by the inventors of the present application in an effort to produce a titanium compound that meets all requirements, that is, formulation of a uniform and transparent catalytic solution, a stable catalytic solution, a catalytic solution having sufficient catalytic activity, production of a high quality polyester, etc., the inventors discovered that a reaction product produced by the reaction of tetrabutyl titanate and trimellitic acid and then by further reacting the reaction product produced above and tributyl phosphate satisfies all of the above requirements, and the polyester produced has a high softening point and also excellent color. The present invention was accomplished as a result of much research based on the above knowledge.

In other words, the present invention is a method for manufacturing a polyester characterized by using a reaction product produced by reacting the phosphorus compound shown in general formula (III) below

$$R_1O-\overset{O}{\underset{OR_3}{\overset{\|}{\underset{|}{P}}}}-OR_2 \quad \cdots\cdots\cdots\cdots (III)$$

[In the formula, R_1, R_2, and R_3 are either hydrogen atoms or alkyl groups, and at least one of R_1, R_2, and R_3 is an alkyl group.]

with a reaction product A of the titanium compound shown in general formula (I) below

$$Ti(OR)_4 \quad \cdots\cdots\cdots\cdots (I)$$

[In the formula, R is an alkyl group.]

and an aromatic polyhydric carboxylic acid shown in general formula (II) below

$$(COOH)_n \quad \cdots\cdots\cdots\cdots (II)$$

[In the formula, n is an integer in the range of 2-4.]
or an anhydride of same as a polycondensation reaction catalyst in production of a polyester by conducting a polycondensation reaction for a glycol ester of at least one type of bifunctional aromatic carboxylic acid and/or a low grade polymer of same in the presence of a catalyst.

The method used for production of the glycol ester of the bifunctional aromatic carboxylic acid used in the present invention is not especially limited. In general, production is achieved by reacting a bifunctional aromatic carboxylic acid or an ester-forming derivative of same with a glycol or an ester- forming derivative of same under heat.

For the bifunctional aromatic carboxylic acid used in this case, terephthalic acid is mainly used and for the ester-forming derivative of same, an alkyl ester, phenyl ester, etc., with 1-4 carbon atoms can be used effectively. Furthermore, bifunctional aromatic carboxylic acids other than terephthalic acid may be used and, for example, isophthalic acid, naphthalene dicarboxylic acid, diphenyl dicarboxylic acid, diphenyl sulfone dicarboxylic acid, diphenyl methane dicarboxylic acid, diphenyl ether dicarboxylic acid, diphenoxy ethane dicarboxylic acid, β-hydroxyethoxy benzoic acid, etc., can be mentioned, and furthermore, a part of the primary bifunctional aromatic carboxylic acid component may be replaced with other bifunctional aromatic carboxylic acids and/or bifunctional aliphatic carboxylic acids such as sebacic acid, adipic acid and oxalic acid, bifunctional alicyclic carboxylic acids such as 1,4-cyclohexane dicarboxylic acid or also ester-forming derivatives of same.

Glycol mainly means ethylene glycol, and for the ester-forming derivatives of same, in /58(particular, ethylene oxide can be used effectively. Furthermore, aliphatic and alicyclic glycols such as tetramethylene glycol, trimethylene glycol, and cyclohexane-1,4-dimethanol may be used as well.

For the method used for production of a glycol ester and/or low grade polymers of same from the aforementioned acid component and glycol component, for example, in the case of an ethylene glycol ester of terephthalic acid and/or a low grade polymer of the same used as a structural raw material of polyethylene terephthalate, a method in which a direct esterification reaction is provided for terephthalic acid and ethylene glycol, a method in which a transesterification reaction is conducted for a lower alkyl ester of terephthalic acid and ethylene glycol or a method in which an adduct reaction is conducted for terephthalic acid with ethylene oxide are commonly used. A given catalyst may be used in the aforementioned reactions, and those with an absence of an adverse effect on the color of the finished product are selected while considering the objective of the present invention.

The polycondensation reaction catalyst used in the method of the present invention is a reaction product produced by the reaction of reaction product A of a titanium compound and an aromatic polyhydric carboxylic acid or an anhydride of same with a phosphorus compound.

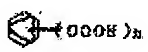
For the titanium compound used in this case, those shown in general formula (I) below [are desirable.]

(I)

$$Ti(OR)_4 \quad \cdots\cdots\cdots (I)$$

The R in the aforementioned general formula is an alkyl group, and in particular, an alkyl group with 3 or 4 carbon atoms. In other words, tetrapropyl titanate, tetraisopropyl titanate and tetrabutyl titanate are desirable. At least two different types of the aforementioned titanium compounds may be used in combination as well.

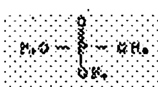
For the aromatic polyhydric carboxylic acid or an anhydride of the same reacted with the aforementioned titanium compound, those shown in general formula (II) below [are desirable].



$\cdots\cdots\cdots$ (II)

n in the general formula is an integer in the range of 2-4 and the compound is a divalent, trivalent, or tetravalent benzene carboxylic acid or an anhydride of same, and in particular, those that enable formation of an anhydride, in other words, phthalic acid, trimellitic acid, hemimellitic acid and pyromellitic acid and anhydrides of same are desirable.

Furthermore, for the phosphorus compound further reacted with reaction product A of the aforementioned titanium compound and an aromatic polyhydric carboxylic acid or an anhydride of same, those shown in general formula (III) below [are desirable].



$\cdots\cdots\cdots$ (III)

In this case R_1, R_2, and R_3 are either hydrogen atoms or alkyl groups, and at least one of R_1, R_2, and R_3 is an alkyl group. In specific terms, monoalkyl esters, dialkyl esters, trialkyl esters or mixed alkyl esters of phosphoric acid are desirable, and esters with an alkyl group with 1-4 carbon atoms are further desirable. Furthermore, the aforementioned phosphorus compound may be used independently or two or more different compounds may be mixed and used in combination.

The reaction between the aforementioned titanium compound and an aromatic polyhydric carboxylic acid or an anhydride of same is achieved by first dissolving a part or all of the aromatic polyhydric carboxylic acid or anhydride of same in a solvent, and by then dropwise adding the titanium compound and reacting for approximately 30 min or longer at a temperature in the range of 0°C-200°C. The reaction pressure used in this case is not especially limited and normal pressure

can be used effectively. Furthermore, for the solvent used in this case, those capable of dissolving a part or all of the aromatic polyhydric carboxylic acid or anhydride of same can be used effectively, and in particular, ethanol, ethylene glycol, benzene, etc., are desirable, and a glycol having the same composition as that used for the glycol component comprising the polyester is especially desirable.

The molar ratio of the titanium compound and the aromatic polyhydric carboxylic acid or anhydride of same used in the aforementioned reaction can be selected from a wide range, but if the ratio of the titanium compound used is too high, the color and softening point of the polyester produced are likely to be inferior, and on the other hand, if the ratio is too low, the polycondensation reaction is less likely to be promoted, and for this reason, the ratio of the aromatic polyhydric carboxylic acid or anhydride of same is preferably in the range of 1/2-2 1/2 moles per 1 mole of the titanium compound.

Reaction product A of the titanium compound and the aromatic polyhydric carboxylic acid or anhydride of same produced as described above may be used for the reaction with a phosphorus compound as is in the form of a solution or it may be first recrystallized with acetone, etc., and subsequently dissolved in a solvent and used for the reaction with the phosphorus compound that /581 follows.

The reaction between reaction product A produced as described above and the phosphorus compound is achieved by dropwise adding the phosphorus compound to a solution of reaction product A and reacting for approximately 30 min at a temperature in the range of 150-200°C. The reaction pressure used in this case is not especially limited and standard pressure can be used effectively. Furthermore, for the solvent used in this case, those used for the reaction between the aforementioned titanium compound and aromatic polyhydric carboxylic acid or anhydride of same can be used effectively, and as in the case of the aforementioned reaction, it is advantageous if the glycol used for the glycol component comprising the present invention is used since the solution formed after the reaction can be used as is, and in particular, this is effective for industrial application.

The amount of phosphorus compound used in the aforementioned reaction can be selected from a wide range, but if the amount of phosphorus compound used is too low, the color and softening point of the polyester produced are likely to be inferior; on the other hand, if the ratio of the phosphorus compound used is too high, the polycondensation reaction is less likely to be promoted, and for this reason, the ratio of the phosphorus compound is preferably in the range of 1/3-6 moles per 1 mole of titanium in reaction product A from the aforementioned titanium compound and aromatic polyhydric carboxylic acid or anhydride of same and a range of 1/2-3 moles is even more desirable.

The amount of reaction product from the aforementioned reaction product A and phosphorus compound produced as described above (hereinafter referred to as titanium compound containing phosphorus) is not especially limited, but if the amount used is too low, an adequate polycondensation reaction rate cannot be achieved; on the other hand, if the aforementioned amount used is too high, yellow color is likely to be produced in the finished polyester product, and for this reason, the aforementioned amount used is in the range of 0.001-0.05 mol%, preferably, in the range of 0.005-0.03 mol%, with respect to the bifunctional aromatic carboxylic acid component used as a raw material of the polyester in terms of the titanium atoms. Furthermore, the addition time is not especially limited as long as the addition is made before completion of the polycondensation reaction, and it is desirable if the addition is made during the period between just before starting to right after starting the polycondensation reaction. Especially if used as a transesterification catalyst, it is desirable if the aforementioned amount is added during the period between just before starting to right after starting the transesterification reaction. And furthermore, an appropriate amount of other polycondensation reaction catalysts, for example, antimony compounds, germanium compounds, etc., can be used in combination as long as reaching the objective of the present invention is not inhibited.

Furthermore, special conditions are not required for the polycondensation reaction used in the present invention, and for example, conditions commonly used in production of standard polyesters by means of a polycondensation reaction of a glycol ester of a bifunctional aromatic carboxylic acid and/or a low grade polymer of same can be used effectively. In the case of polyethylene terephthalate, in general, a method in which a polycondensation reaction is conducted for an ethylene ester of a bifunctional aromatic carboxylic acid and/or a low grade polymer of same with the aforementioned amount of the titanium compound containing phosphorus added while heating to a temperature between the melting point of the aforementioned material and 300°C with the generated glycol removed under vacuum can be used. And furthermore, if a titanium compound containing phosphorus is used as a transesterification reaction catalyst, special conditions are not required for the transesterification reaction, and for example, in the case of polyethylene terephthalate, heating is provided for the reaction mixture with the aforementioned amount of titanium compound containing phosphorus added (a mixture of a lower alkyl ester of terephthalic acid and ethylene glycol or a mixture of the same and a reaction product of the same) under normal pressure, or under slight pressure (in general, approximately 10 kg/cm^2 or less) or under a slight vacuum (in general, up to approximately 50 mmHg) to a temperature in the range of 150-250°C and the alcohol generated is distilled and the transesterification reaction is carried out, and then the polycondensation reaction is completed.

And furthermore, upon application of the present invention, a monofunctional compound, for example, benzyl benzoic acid, phenol sulfonate, γ-hydroxypropane sulfonic acid, etc., may be

bonded to the end of the produced polyester, and furthermore, the produced polyester may be copolymerized with an appropriate amount of a trifunctional or higher polyfunctional compound that does not interfere with the thermoplastic performance of the produced polyester.

And furthermore, in this case, desired additives, for example, coloring matter, matting agents, fluorescent whiteners, stabilizers, ultraviolet absorbers, ether bond inhibitors, dye promoters, flame retardants, antistatic agents, etc., also may be included, as needed.

The present invention is explained in further detail with the application examples below. "Parts" in the application examples is parts by weight, and [η] is the ultimate viscosity obtained by measuring the viscosity at 35°C with orthochlorophenol as the solvent. The color tone is shown /58
as the L value and b value obtained by measuring the surface color by a color machine, Model CM-20 (product of Color Machine Co. Ltd.) after providing a heat-treatment for the polymer for 20 min at a temperature of 200°C in flowing nitrogen for crystallization. The L value represents the color value and the greater the number, the higher the color value, and furthermore, the higher the b value toward the (+) side, the greater the degree of yellow, and the higher the value toward the (-) side, the greater the degree of blue. In this case, the softening point was measured using the penetration method.

Application Example 1

(a) Adjustment of Catalyst

380 parts of ethylene glycol, 35 parts of tetrabutyl titanate and 39 parts of trimellitic anhydride (2 molar times the tetrabutyl titanate) were charged to a reactor equipped with a stirring device, fractionating tower, and butanol distillation condenser, and heated to a temperature in the range of 150-180°C under normal pressure, and a reaction was carried out for 60 min while the butyl alcohol and ethylene glycol monobutyl ether generated as a result of the reaction were distilled outside the system, and when 31 parts of distillate were obtained, the reaction was stopped and the system cooled to room temperature.

Furthermore, 187 parts of the produced reaction solution were extracted; then, 222 parts of tributyl phosphate (2 molar times with respect to the titanium atoms included in the reaction solution) were added dropwise in the air and at room temperature while stirring was provided. Heating was provided after the aforementioned addition was completed, and in this case, distillation of ethylene glycol monobutyl ether was achieved close to the internal temperature which was in the range of 170-180°C. The aforementioned reaction was stopped when an internal temperature of 195°C was achieved and the material was cooled to room temperature. As a result, a transparent catalytic solution with a light yellow tint was produced.

(b) Production of Polyester

970 parts of dimethyl terephthalate, 640 parts of ethylene glycol, 0.18 parts of manganese acetate and 0.12 parts of cobalt acetate were charged to a reactor equipped with a stirring device, fractionating tower and methanol distillation condenser, the temperature was increased from 140°C to 230°C, and a transesterification reaction was conducted while the methanol generated as a result of the aforementioned reaction was distilled outside the system. In this case, 3 h after starting the reaction, an internal temperature of 230°C was achieved, and 320 parts of methanol were distilled.

In this case, as a stabilizer, 0.21 parts of trimethyl phosphate was added and as a matting agent, 4.85 parts of titanium dioxide were added, and furthermore, the catalytic solution produced in the aforementioned method (a) was added in an amount such that 0.015 mol% of titanium atoms were present with respect to the dimethyl terephthalate in solution. Furthermore, the aforementioned reaction mixture was transferred to a reactor equipped with a stirring device and an ethylene glycol distillation condenser, and then a polycondensation reaction was conducted while the temperature was slowly increased from 230°C to 285°C and the pressure was reduced from standard pressure to a high vacuum of 1 mm Hg. The total polycondensation reaction time required was 3 h and 30 min, and as a result, a polymer having an ultimate viscosity [η] of 0.642 was produced. The softening point of the aforementioned polymer was 260.7°C, and the color value had an L value of 82.6 and a b value of 2.3.

Furthermore, for comparison, instead of the catalytic solution produced in the aforementioned method (a), 0.26 parts of tetrabutyl titanate (0.015 mol% with respect to the dimethyl terephthalate in the form of titanium atoms) was used and a reaction was conducted according to the method described in the method (b) above. The polymer produced had an [η] of 0.648, the color value had an L value of 78.3 and a b value of 11.7, and the softening point was 259.1°C.

Application Example 2

The amount of tributyl phosphate used in the method of Application Example 1-(a) was changed to the various amounts listed in Table 1 below, and a reaction was conducted as in the method of Application Example 1-(a) above to produce different transparent catalytic solutions. Each catalytic solution was used in an amount of 0.015 mol% of titanium atoms with respect to the dimethyl terephthalate in the solution and polymers were produced as in the case of the aforementioned method of Application Example 1-(b). The results obtained are shown in Table 1 below.

Table 1

実験番号	トリブチルホスフェート量 (モル)	ポリマー特性			
		[η]	軟化点 (℃)	色調 L	色調 b
2-1	0.2	0.655	259.3	79.2	10.1
2-2	0.5	0.658	261.2	82.4	5.5
2-3	1	0.662	260.9	81.0	5.6
2-4	4	0.651	260.3	82.3	2.0
2-5	10	0.432	257.9	82.8	1.5

Key:
1 Test No.
2 Amount of tributyl phosphate (moles)
3 Properties of polymer
4 Softening point
5 Color tone

The molar ratio of tributyl phosphate in the aforementioned table shows the molar ratio /58: with respect to 1 mole of titanium atoms included in the catalytic solution.

<u>Application Examples 3 and 4</u>

Instead of the tributyl phosphate used in Application Example 1-(a), trimethyl phosphate and dibutyl phosphate were each used in amounts shown in Table 2 below and a reaction was conducted as in Application Example 1-(a) to produce transparent catalytic solutions with a light yellow tint. Each catalytic solution was used in an amount of 0.015 mol% of titanium atoms with respect to the dimethyl terephthalate in the solution and polymers were produced as in the aforementioned method of application example 1-(b). The results obtained are shown in Table 2 below.

Table 2

	リン化合物		ポリマー物性			
	種類	量 (モル)	(η)	軟化点 (℃)	色調 L	色調 b
実施例3	トリメチルホスフェート	2	0.669	263.0	80.0	2.1
〃 4	ジブチルホスフェート	2	0.663	260.8	82.4	1.8

Key:
1 Phosphorus compound
2 Polymer properties
3 Type
4 Amount (moles)
5 Softening point
6 Color tone
7 Application Example 3
8 Trimethyl phosphate
9 Dibutyl phosphate

The molar ratio of the phosphorus compound in the aforementioned table shows the molar ratio for 1 mole of titanium atoms included in the catalytic solution.